

Local structure of $RE\text{FeAsO}$ ($RE=\text{La, Pr, Nd, Sm}$) oxypnictides studied by Fe K-edge EXAFS

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Abstract.

Local structure of $RE\text{FeAs}$ ($RE=\text{La, Pr, Nd, Sm}$) system has been studied as a function of chemical pressure varied due to different rare-earth size. Fe K-edge extended X-ray absorption fine structure (EXAFS) measurements in the fluorescence mode has permitted to compare systematically the inter-atomic distances and their mean square relative displacements (MSRD). We find that the Fe-As bond length and the corresponding MSRD hardly show any change, suggesting the strongly covalent nature of this bond, while the Fe-Fe and Fe-RE bond lengths decrease with decreasing rare earth size. The results provide important information on the atomic correlations that could have direct implication on the superconductivity and magnetism of $RE\text{FeAs}$ system, with the chemical pressure being a key ingredient.

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The recent discovery of high T_c superconductivity in the LaOFeAs [1] has triggered intensive research activities on REOFeAs (RE=rare earth) oxypnictides, producing a large number of publications focusing on different aspects of these materials [2, 3, 4]. One of the interesting aspects of these materials is the competing spin density wave (SDW) and the superconductivity [5, 6, 7]. Indeed, the undoped compound REOFeAs is antiferromagnetically ordered (albeit a poor metal), and shows a structural phase transition [5, 6, 7, 8, 9, 10, 11]. With doping, the system gets superconducting and the structural transition as well as the SDW transition disappears [2, 3, 4]. In addition, while the maximum T_c of the doped system increases with reducing the rare-earth ion size [2, 3, 4, ?, 13], the structural transition temperature decreases for the undoped system [5, 6, 7, 8, 9, 10, 11]. These observations show interesting interplay between structure, magnetism and superconductivity with the chemical pressure and structural topology being important parameters.

It is known that a mere knowledge of the long range ordered structure is generally insufficient to describe electronic functions of a system with interplaying electronic degrees of freedom. Indeed, this has been shown for transition metal oxides in which the electronic functions like superconductivity, colossal magneto resistance and metal insulator transitions are related with interplaying charge- spin lattice degrees of freedom [14]. Therefore, a detailed knowledge of the atomic structure for the REOFeAs oxypnictides could be a timely feedback to the theoretical models for correlating structure, magnetism and superconductivity in these materials.

Extended X-ray absorption fine structure (EXAFS) is a site selective method, providing information on the local atomic distribution around a selected absorbing atom through photoelectron scattering [15]. Recently, Zhang et al [16] have studied local structure of doped and undoped LaOFeAs system by Fe K-edge and As K-edge measurements, providing a temperature dependent anomaly in the Fe-As correlations at low temperature. This study was followed by Tyson et al [17] measuring the same system using Fe K-edge with no evidence of such anomalies. Here we have decided to address a different aspect and exploited the Fe K-edge EXAFS to explore the local structure of REOFeAs with varying rare-earth size (RE=La (1.16 Å), Pr(1.13 Å), Nd(1.11 Å), Sm(1.08 Å)). The results reveal strongly covalent nature of the Fe-As bond, showing hardly any change with rare earth size, while the Fe-Fe and Fe-RE bonds show a systematic size dependence. On the other hand, the mean square relative displacements (MSRD) determined by the correlated Debye Waller (DW) factors of the Fe-Fe bond length decrease with decreasing rare-earth size and that of Fe-RE seems to increase. Again, the MSRD of Fe-As bond remains almost unchanged with the chemical pressure, underlining the stiffness of this bond.

Fe K-edge X-ray absorption measurements were performed on powder samples of REOFeAs (RE=La, Pr, Nd, Sm) prepared using solid state reaction method [18]. Prior to the absorption measurements, the samples were characterized for the phase purity and the average structure by X-ray diffraction measurements [9]. The X-ray absorption measurements were made at the beamline BM29 of the European Synchrotron Radiation

Facility (ESRF), Grenoble, where the synchrotron radiation emitted by a bending magnet source at the 6 GeV ESRF storage ring was monochromatized using a double crystal Si(311) monochromator. The Fe K_α fluorescence yield was collected using a multi-element Ge detector array. Simultaneous transmission signal was measured to make sure the observed signal to represent true X-ray absorption, however, it was not possible to obtain absorption signal in transmission mode without a contribution of the rare-earth L_{II}-edge (6.267KeV, 6.835 KeV, 7.126 KeV and 7.737 KeV respectively for the La, Pr, Nd and Sm with respect to the Fe K-edge at 7.112 KeV) and hence the choice was to opt for the partial absorption signal measured by fluorescence detection for a systematic comparison. The samples were mounted in a continuous flow He cryostat to perform the measurements at low temperature (40 K). The sample temperature was controlled and monitored within an accuracy of ± 1 K. Several absorption scans were measured to ensure reproducibility of the spectra and a high signal to noise ratio. Standard procedure was used to extract the EXAFS signal from the absorption spectrum [15], followed by the X-ray fluorescence self-absorption correction before the analysis.

Figure 1 shows Fe K-edge EXAFS oscillations of REOFeAs samples at low temperature (40 K) extracted from the X-ray absorption spectra measured on the powder samples. The EXAFS oscillations are weighted by k^2 to highlight the higher k -region. There are evident differences between the EXAFS oscillations due to differing local structure of REOFeAs with different RE atom (see e.g. the oscillation around $k=6-8 \text{ \AA}^{-1}$ and in the k range above $\sim 10-14 \text{ \AA}^{-1}$). The differences in the local structure could be better appreciated in the Fourier transforms of the EXAFS oscillations providing real space information.

Figure 2 shows magnitude of the Fourier transforms, $|\text{FT}(k^2\chi(k))|$. The Fourier transforms are not corrected for the phase shifts due to the photoelectron back-scattering and represent raw experimental data. The main peak at $\sim 2.4 \text{ \AA}$ is due to Fe-As (4 As atoms at a distance $\sim 2.4 \text{ \AA}$) and Fe-Fe (4 Fe atoms at a distance $\sim 2.8 \text{ \AA}$) bond lengths, while the peak at $\sim 3.6 \text{ \AA}$ corresponds to the Fe-RE bond length (4 RE atoms at a distance $\sim 3.72 \text{ \AA}$). While the main Fourier transform peak at $\sim 2.4 \text{ \AA}$ appears to shift towards higher R-values, the Fe-RE peak seems to appear with a decreased amplitude with decreasing rare-earth size. The evident shift of the main peak is due to increased amplitude of the Fe-Fe scattering derived by decreasing Fe-Fe bond length and corresponding MSRD (discussed later).

The EXAFS amplitude depends on several factors and could be given by the following general equation[15]:

$$\chi(k) = \sum_i \frac{N_i S_0^2}{k R_i^2} f_i(k, R_i) e^{-\frac{2R_i}{\lambda}} e^{-2k^2\sigma_i^2} \sin[2kR_i + \delta_i(k)] \quad (1)$$

Here N_i is the number of neighboring atoms at a distance R_i . S_0^2 is the passive electrons reduction factor, $f_i(k, R_i)$ is the backscattering amplitude, λ is the photoelectron mean free path, and σ_i^2 is the correlated Debye-Waller (DW) factor, measuring the mean square relative displacements (MSRD) of the photoabsorber-

backscatterer pairs. Apart from these, the photoelectron energy origin E_0 and the phase shifts δ_i should be known.

We have used conventional procedure to analyze the EXAFS signal [15] due to three shells, i.e., Fe-As, Fe-Fe and Fe-RE scatterings. Except the radial distances R_i and the corresponding DW factors σ_i^2 , all other parameters were kept fixed in the least squares fit ($S_0^2=1$). The EXCURVE9.275 code was used for the model fit with calculated backscattering amplitudes and phase shift functions [19]. The number of independent data points, $N_{ind} \sim (2\Delta k \Delta R)/\pi$ [15] was 16 for the present analysis ($\Delta k=11 \text{ \AA}^{-1}$ ($k=3\text{-}14 \text{ \AA}^{-1}$) and $\Delta R=2.5 \text{ \AA}$). Starting parameters were taken from the diffraction studies [5, 6, 7, 8, 9, 10, 11, 20]. A representative three shell model fit is shown with experimental Fourier transform as inset to the Figure 2.

The average radial distances as a function of rare earth atom are shown in Figure 3. There is a gradual decrease of the average Fe-Fe and Fe-RE distances (two upper panels) with decreasing rare earth size, consistent with the diffraction studies showing decreasing lattice parameters (the a-axis and c-axis as a function of the rare earth atom are shown as insets) [20]. On the other hand, the Fe-As distance (lower middle panel) does not show any appreciable change with the rare-earth atom size, revealing strongly covalent nature of this bond. Within experimental uncertainties this appears to be consistent with the diffraction results [5, 6, 7, 8, 9, 10, 11, 13].

Using the bond lengths measured by EXAFS, we can determine directly the opening angle at the top of the Fe_4As tetrahedron (Fe-As-Fe angle θ_3), considered to be the key to the superconductivity in these materials [5]. The Fe-As-Fe angle θ_3 has been calculated using the formula; $\theta_3=\pi-2\cos^{-1}\left(\frac{d_{\text{Fe-Fe}}}{\sqrt{2}d_{\text{Fe-As}}}\right)$. The Fe-As-Fe angle θ_3 is shown in Fig. 3. The Fe-As-Fe angle θ_3 is consistent with the earlier studies, revealing perfect Fe_4As tetrahedron [13, 5] for the SmOFeAs .

Figure 4 shows the correlated DW factors as a function of rare earth atoms measuring the MSRD of different bond lengths. The MSRD of the Fe-Fe (middle panel) and Fe-RE pairs (upper panel) appear to depend on the rare-earth size, while we could hardly see any change in that of the Fe-As pairs indicating again the stiffness of the later. The MSRD of the Fe-Fe shows a clear decrease with decreasing rare earth size, as the Fe-Fe bond length (Fig. 3). Incidentally, the MSRD of the Fe-RE appears to show a small increase with decreasing rare earth size, albeit the change is smaller than that of the Fe-Fe bond length (upper panel).

Recently Tyson et al [17] have reported temperature dependence of Fe-As MSRD for the doped and undoped LaOFeAs , showing that, while the Einstein frequency of the Fe-As mode does not change with doping, there is a small decrease of static contribution to the MSRD. The results of Tyson et al [17] are consistent with strongly covalent nature of the Fe-As bond length. On the other hand, the same authors have shown increased Einstein frequency with doping for the Fe-Fe pair, indicating enhanced Fe-Fe correlations.

In summary, we have measured the local structure of REOFeAs with variable rare-earth ion (RE) revealing highly covalent nature of the Fe-As bond length. In

addition, the Fe-Fe and Fe-RE local atomic correlations show a systematic change with the rare earth ion size, evidenced by MSRD of the respective bond lengths. Considering the conventional superconductivity mechanism in the strong coupling limit [21, 22], the electron-phonon interaction parameter is inversely proportional to the phonon frequency, i.e., proportional to the MSRD (the zero point motion dominates at low temperature and hence $\sigma^2 \approx \hbar/2\omega_E m_r$, where m_r is the reduced mass and ω_E is the Einstein frequency of the pair). Since the T_c of the REFeAs (if doped) increases with decreasing rare earth size, it is reasonable to think that the Fe-Fe phonon modes may not have a direct role in the superconductivity (Fe-Fe MSRD decrease with decreasing rare-earth size). In contrast, the Fe-RE MSRD tends to show a small increase (or remains constant) with decreasing rare earth size, and may be somehow contributing to the superconductivity, however, more experiments are needed to address this issue. Although, it is difficult quantify role of local electron-phonon coupling in the correlating magnetism and superconductivity, the presented results certainly provide timely experimental information on the local atomic fluctuations, that could be important feed-back for new models to describe fundamental properties of the REFeAs with doping and chemical pressure.

Acknowledgments

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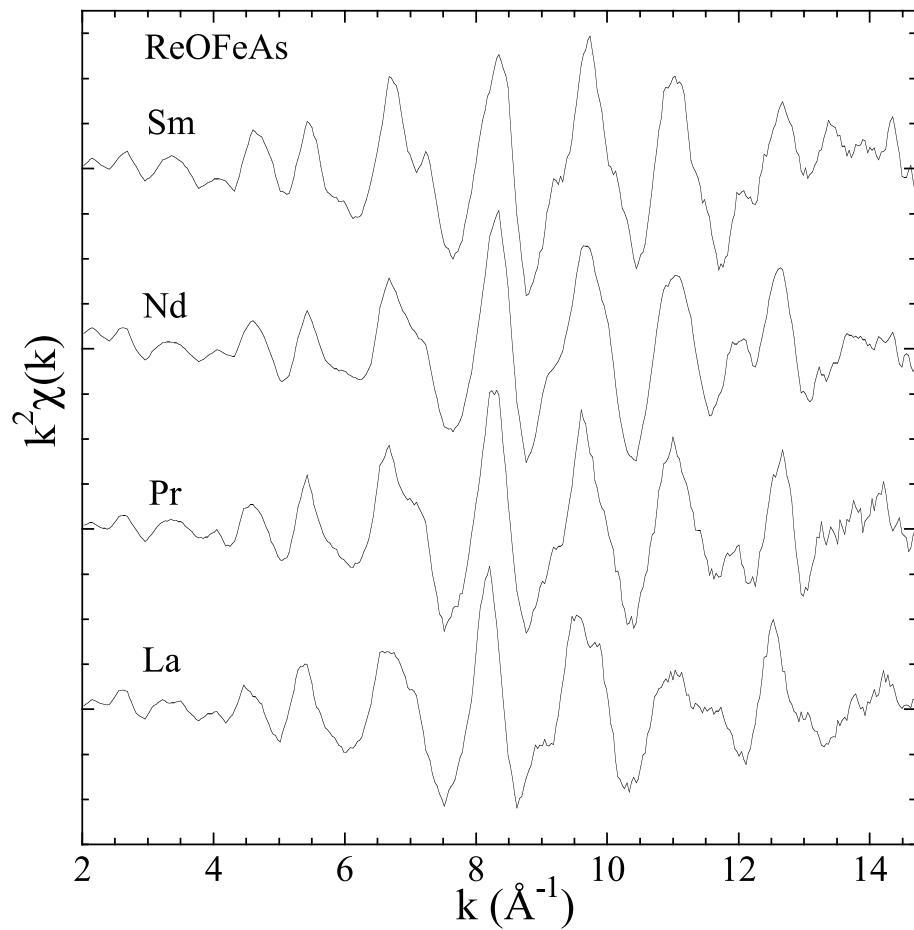


Figure 1. EXAFS oscillations (multiplied by k^2) extracted from the Fe K-edge absorption spectra measured on REOFeAs system ($RE =La, Pr, Nd, Sm$) at low temperature (40 K) and corrected for the fluorescence self-absorption effect.

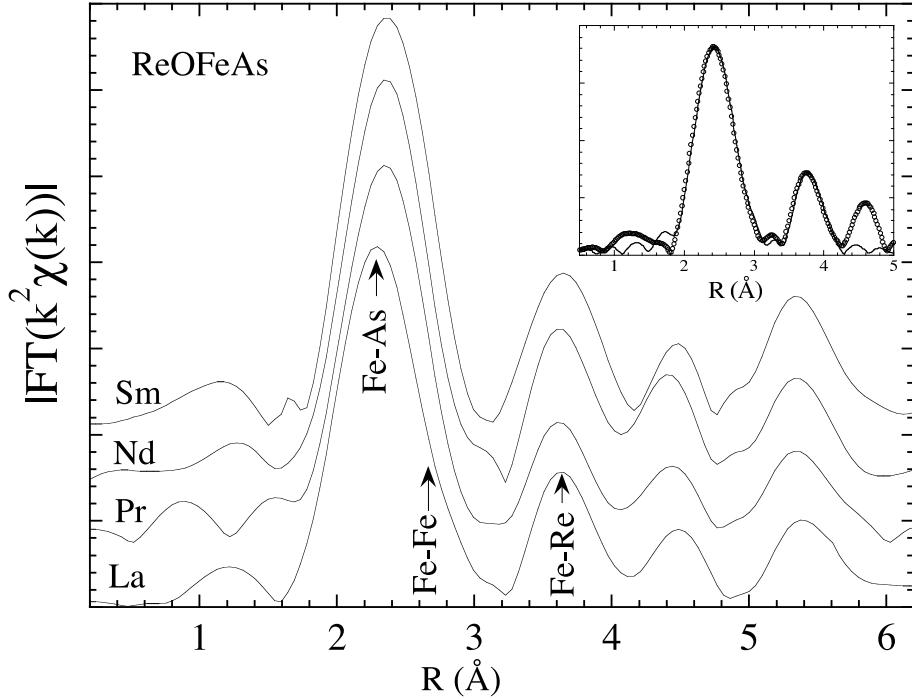


Figure 2. Fourier transforms of the Fe K-edge EXAFS oscillations showing partial atomic distribution around the Fe in the REOFeAs system. The Fourier transforms are performed between $k_{min}=3 \text{ \AA}^{-1}$ and $k_{max}=14 \text{ \AA}^{-1}$ using a Gaussian window. The peak positions do not represent the real distances as the FTs are not corrected for the phase shifts. The inset shows a phase corrected Fourier transform (symbols) (for the LaOFeAs) with a fit over three shells, i.e., Fe-As, Fe-Fe and Fe-Re.

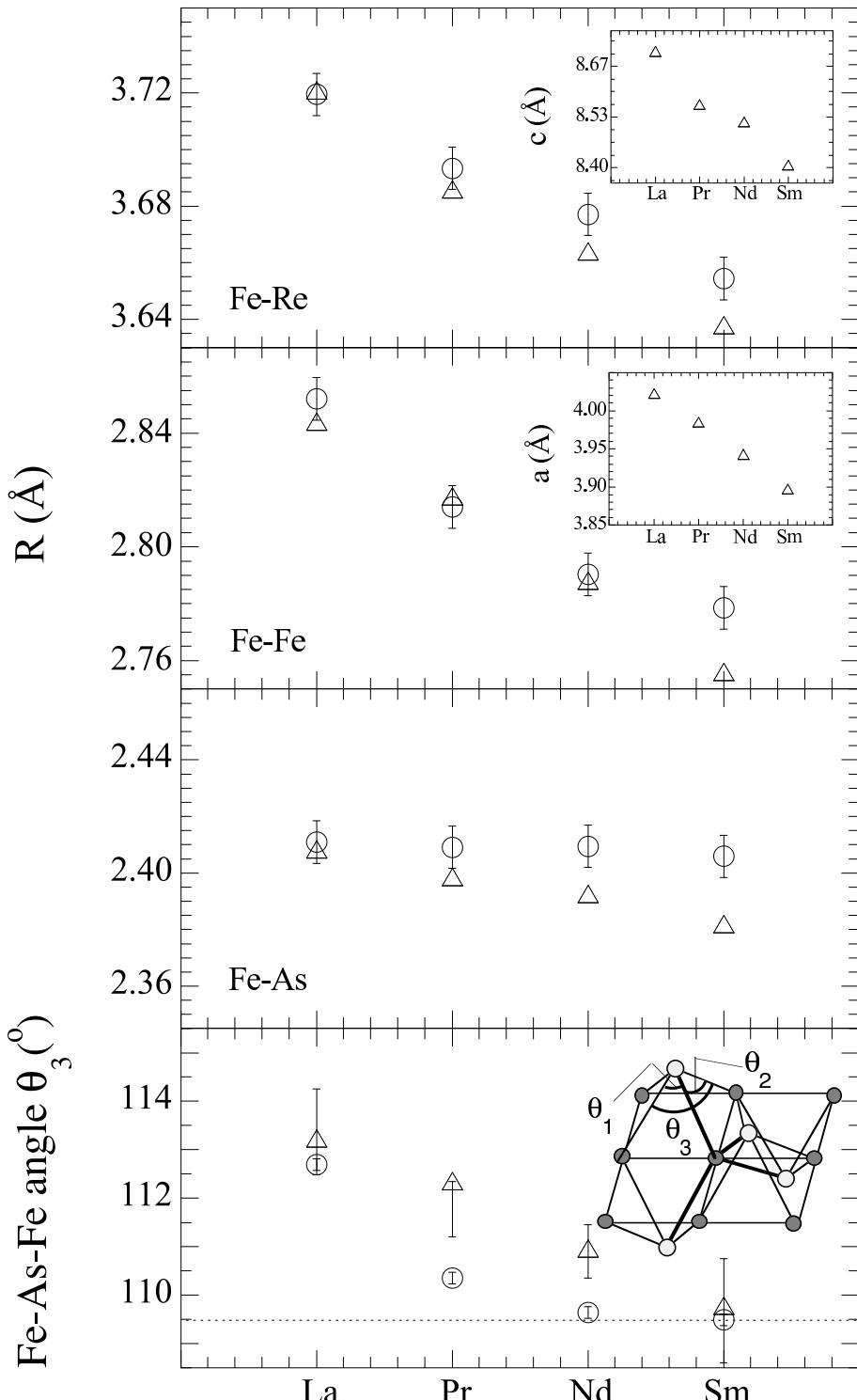


Figure 3. Fe-As (lower middle), Fe-Fe (upper middle) and Fe-RE (upper) distances at 40 K as a function of rare-earth atom. While the Fe-As bond lengths hardly show any change, the Fe-Fe and Fe-RE bonds change with rare earth size. The insets (two upper panels) show shrinkage of the lattice parameters with the decreasing rare-earth size [20, 9]. The bond lengths derived from the diffraction are included in the three panels for the comparison. Error bars represent the average uncertainties estimated by creating correlation maps. The Fe-As-Fe angle θ_3 determined using the EXAFS data (circles) is also shown (lower) with the dotted line at $\theta_3=109.5^\circ$ corresponding to a perfect tetrahedron. The θ_3 determined from the diffraction data is shown for comparison (triangles). The vertical bars in the lower panel represent the span of the θ_3 values from the EXAFS data.

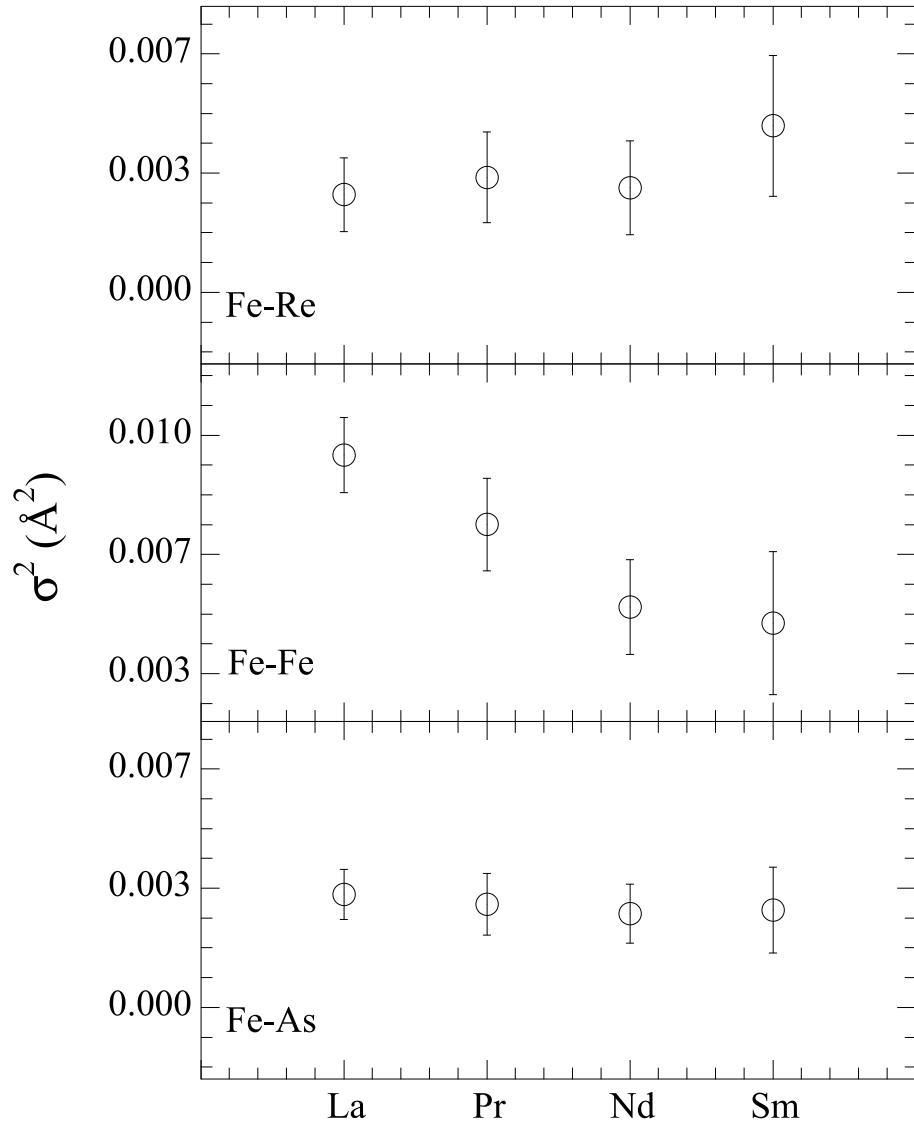


Figure 4. Mean square relative displacements (MSRD) of the Fe-As (lower), Fe-Fe (middle) and Fe-RE (upper) pairs at 40 K as a function of rare-earth size. As the bond length (Fig. 3), the MSRD of Fe-As hardly show any change indicating strongly covalent nature of this bond. On the other hand, the MSRD of Fe-Fe shows a decrease while that of the Fe-RE tending to increase from $LaOFeAs$ to $SmOFeAs$.